The Development of Organic Conductors, Including Semiconductors, Metals and Superconductors

Lessons from History

Organic Electronic (MOLECULAR) Materials

Design

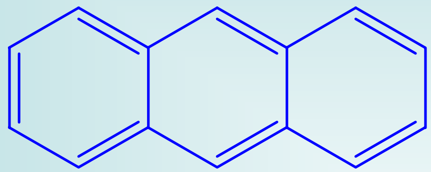
↓

Ensemble

↓

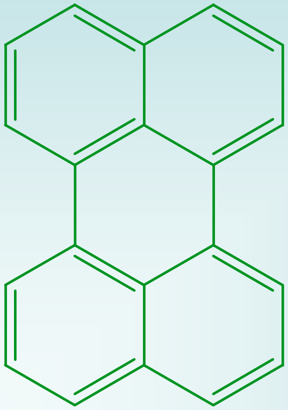
Properties

Organic Conductors, Early History
Charge Carrier Generation: Electron Donors



Pochettino, A., *Accad. Lincei Rend.*, **1906**, *15*, 171

Photogeneration



Perylene (Per)

facile oxidation

$Per(I_2)_3$ $\sigma_{RT} = 0.5$ S/cm

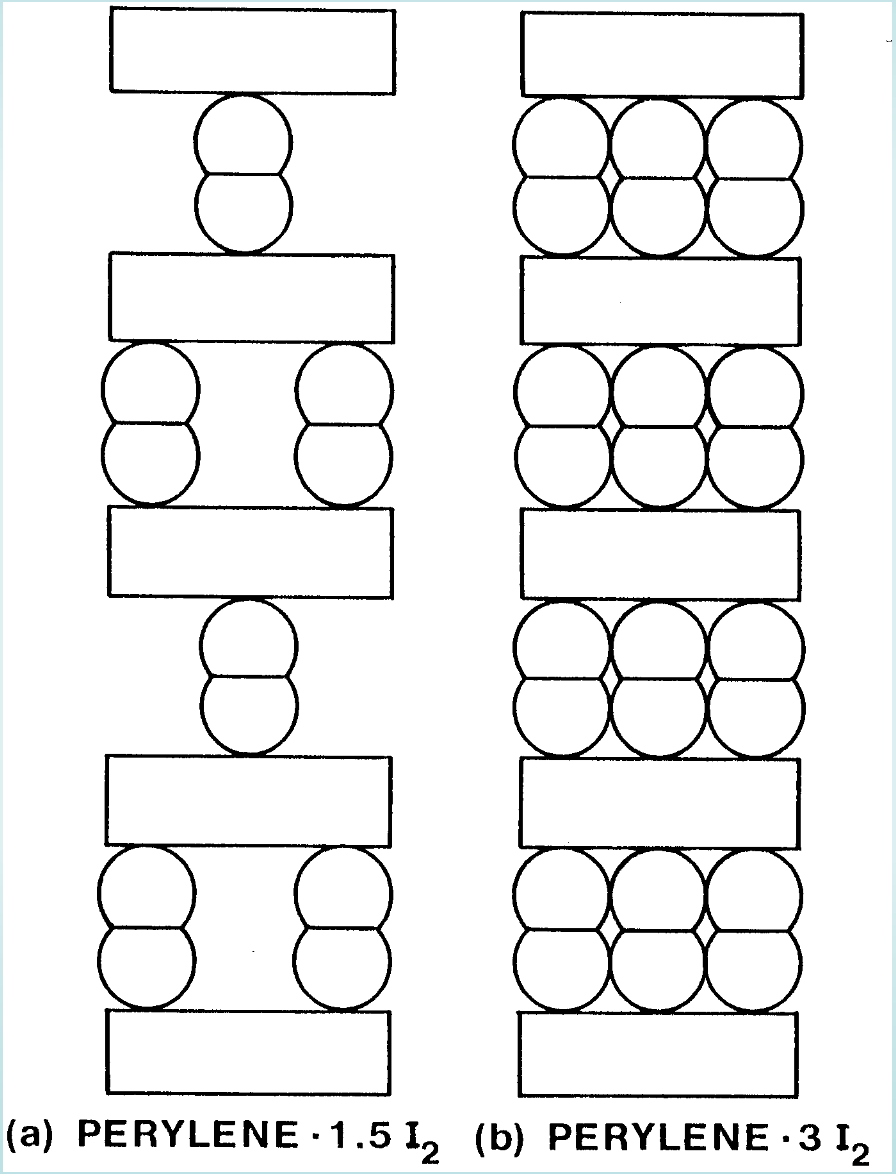
Akamatu, H.; Inokuchi, H.; Matsunaga, Y. *Nature*, **1954**, *173*, 168

Labes, M. M., et al *Proc. Int. Conf. Semicon. Phys.* Prague **1960**, p 850

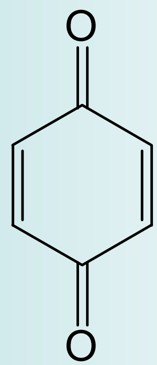
$Per(I_2)_4$ $\sigma_{RT} = 30 - 50$ S/cm (metal to ca 270K)

Labes, M. M., et al *J. Chem. Soc. Chem. Commun.* **1979**, 329

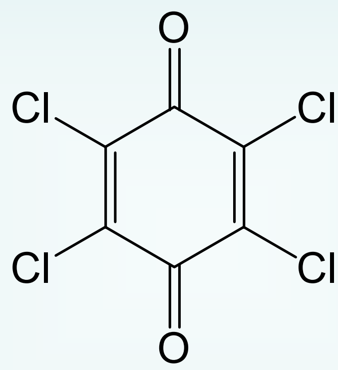
Proposed Structure of Perylene Iodides



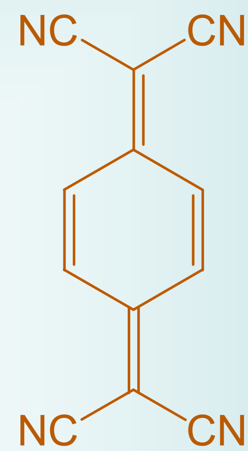
Charge Generation: Electron Acceptors, Acceptor Repertoire



Quinone



Chloranil



TCNQ

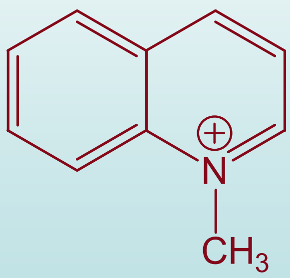
facile reduction

Acker, D. S.; Blomstrom, D. C., *J. Am. Chem. Soc.*, **1962**, *84*, 3370

Types of C-T Complexes

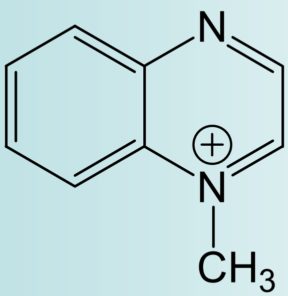
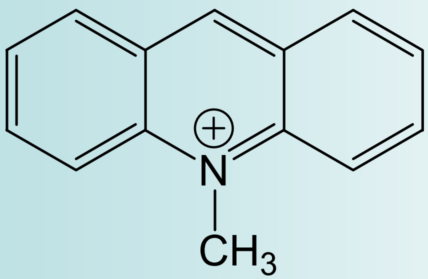
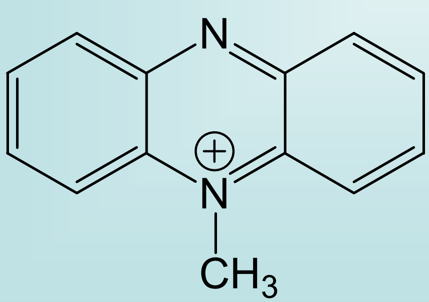
Simple	Complex
$D_{(1)}T_{(1)}$	DnTm
$\sigma_{RT} = 10^{-12} - 10^{-6}$	$\sigma_{RT} = 10 - 100$
e.g. Li TCNQ	e.g. Q $TCNQ_2$

Q =

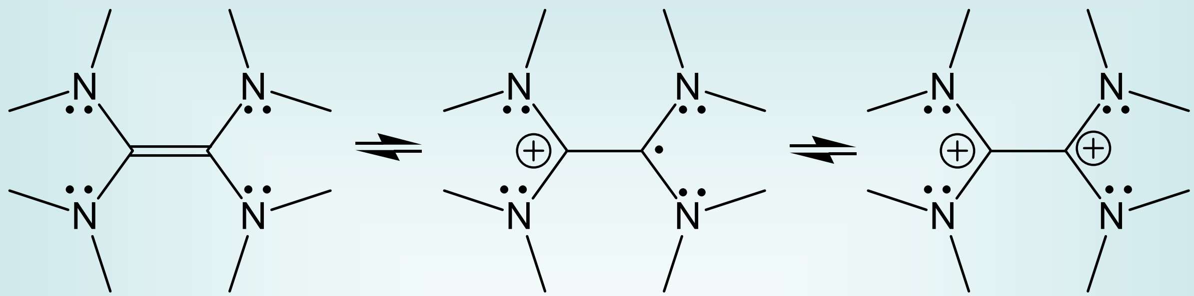


Conductivities of Simpe and Complex TCNQ Salts

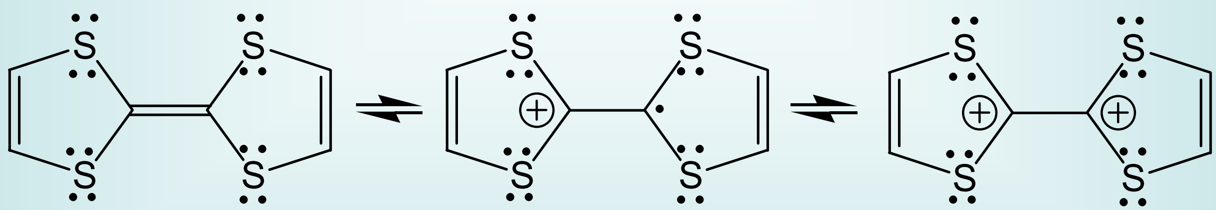
(Scm^{-1})

Cation	Simple	Complex
	10^{-8}	$\approx 10^{2}$
	10^{-14}	$\approx 10^{-1}$
	**10^{2}**	$\approx$**10^{-1}**

The Birth of TTF

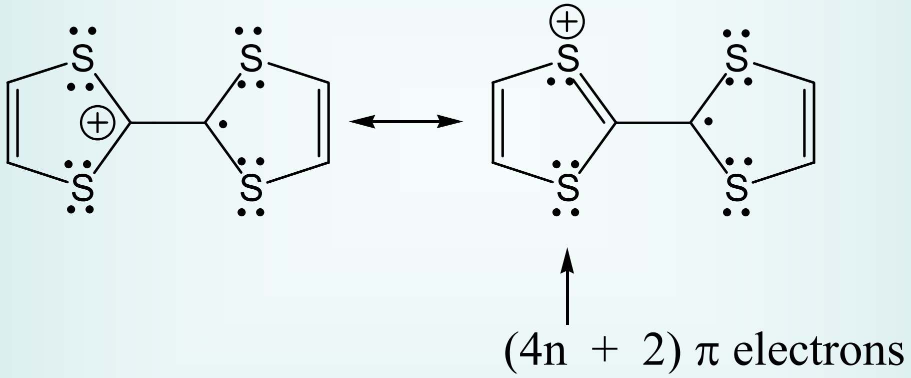


TDAE

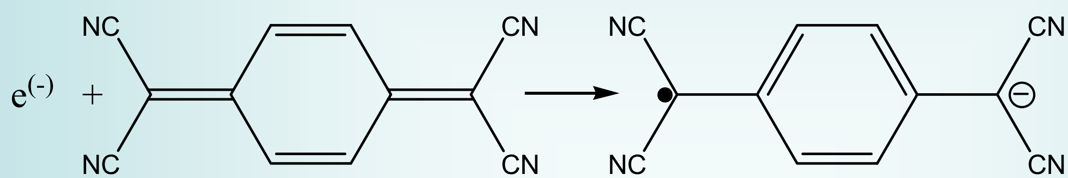


Wudl, F.; Smith, G. M.; Hufnagel, E. J. *Chem. Commun.* **1970**, 1453–1454.
Wudl, F.; Wobschall, D.; Hufnagel, E. J. *J. Am. Chem. Soc.* **1972**, *94,* 670–672.

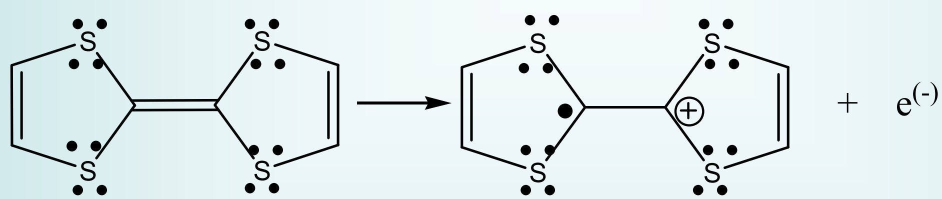
An Important Design Feature



The Marriage of TTF & TCNQ

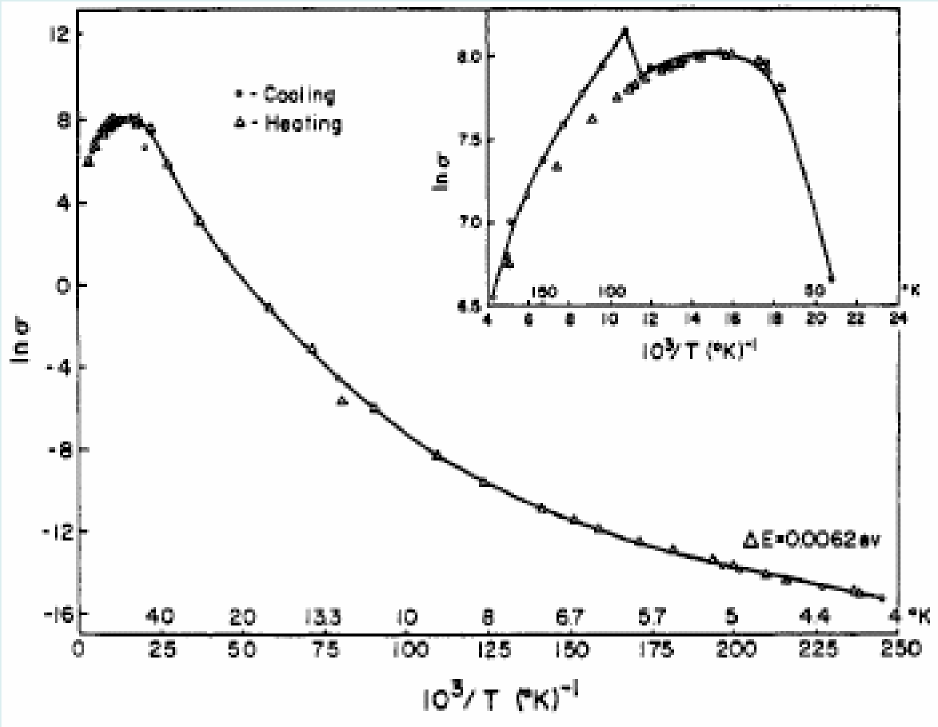


$E_{1/2}$ = 0.22 vs SCE



$E_{1/2}$ = 0.37 vs SCE

TTF-TCNQ, The First Organic Metal



John Ferraris, D. 0. Cowan, V. Walatka, Jr., J. H. Perlstein *J. Am. Chem. Soc.* **1973**, *95*, 948.

The "Giant Conductivity Peak" Phenomenon

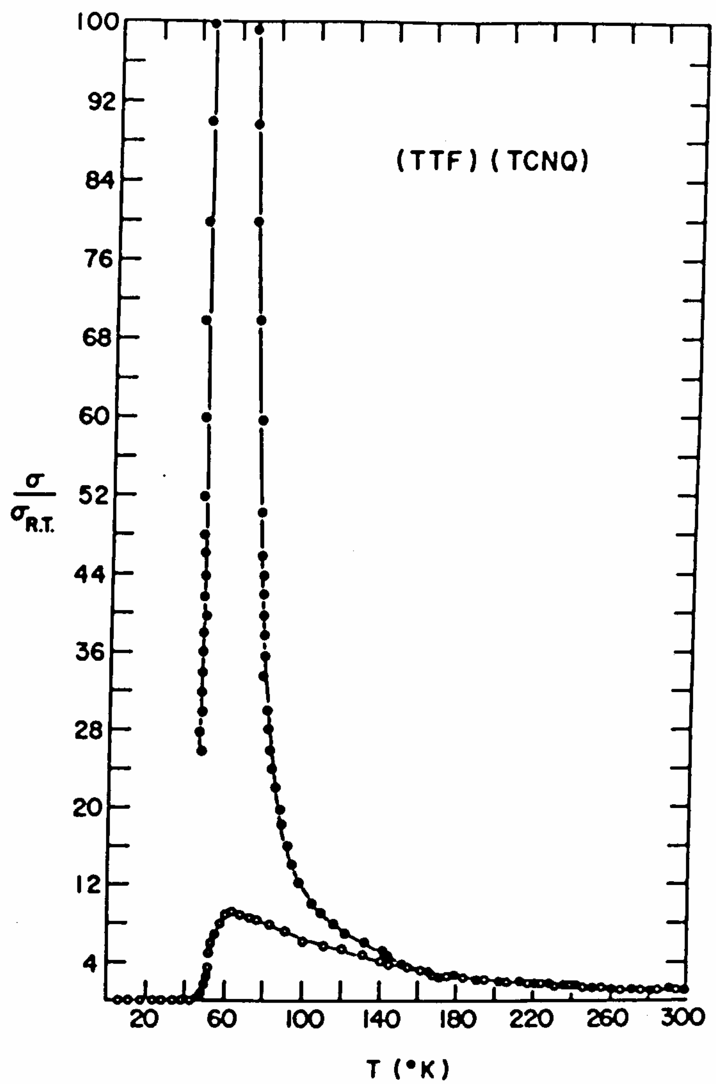


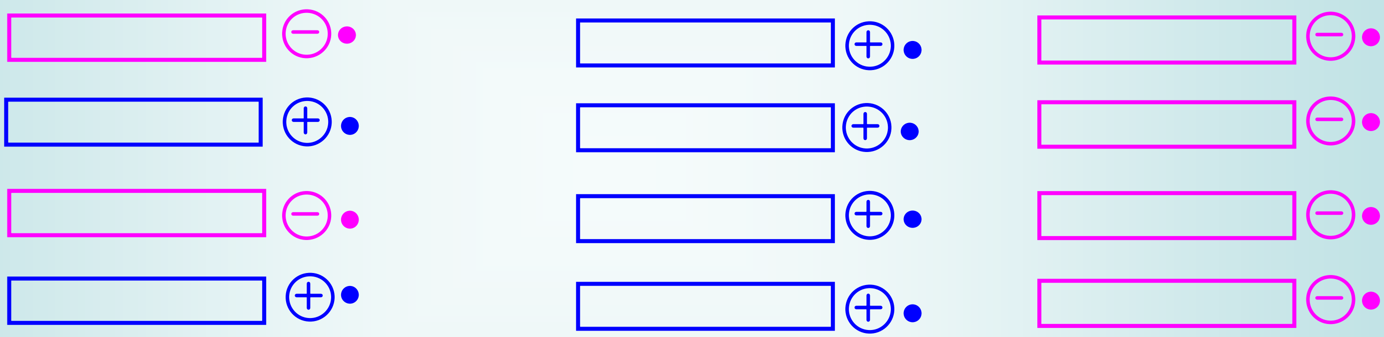
FIG. 3. Temperature dependence of the conductivity of (TTF) (TCNQ) single crystal (– ● – ● –) and of (TTF) (TCNQ) typical crystals (– ○ – ○ –).

Coleman, et al, *Sol. State Commun.* **1973**, *12*, 1125 - 1132

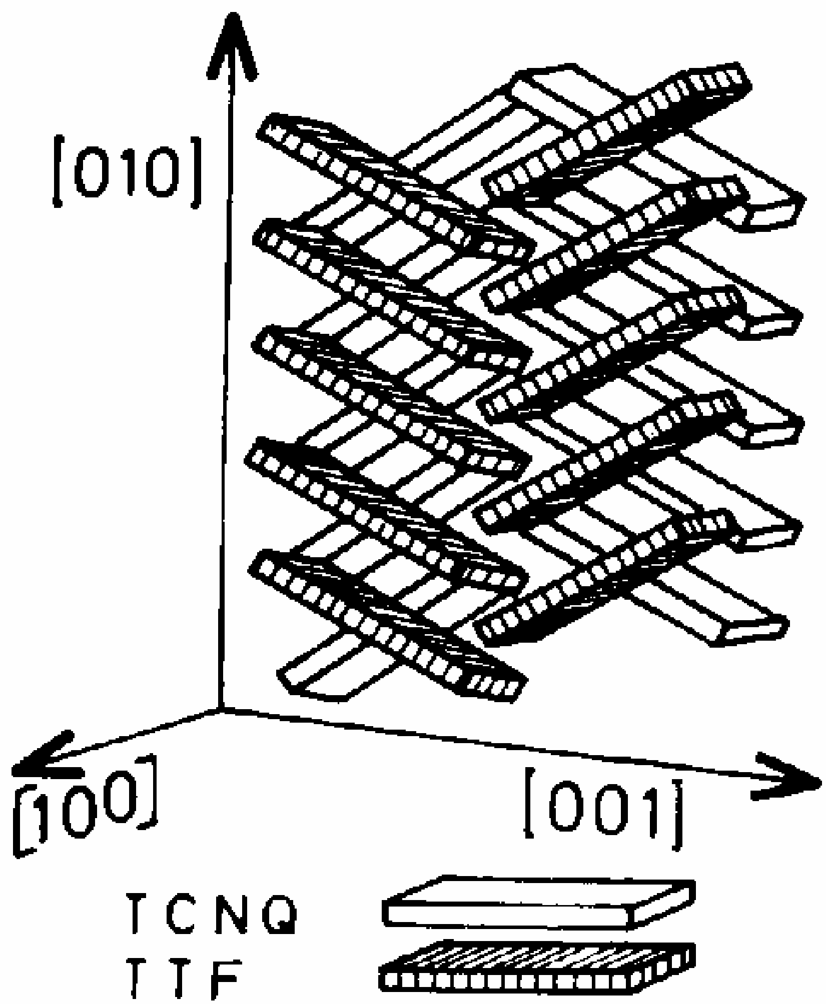
Two Possibilities of Flat Molecule Ensembles

Alternating Stack

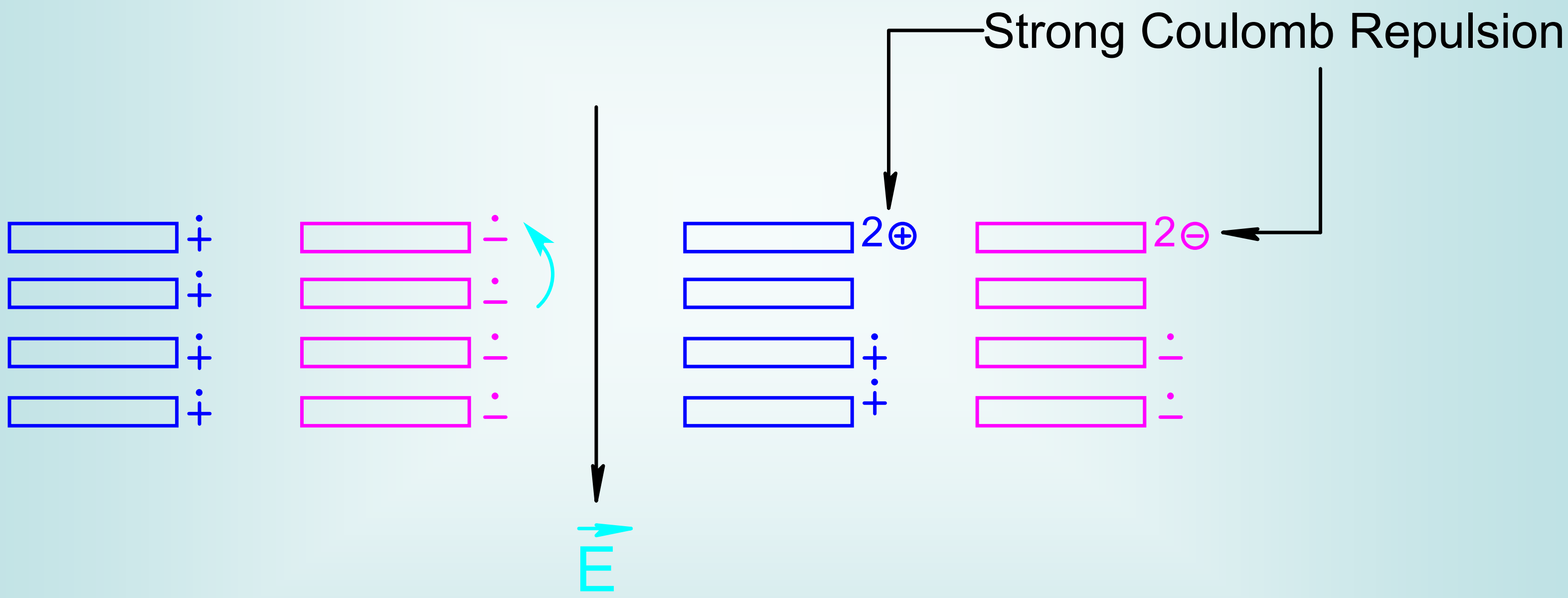
Segregated Stack



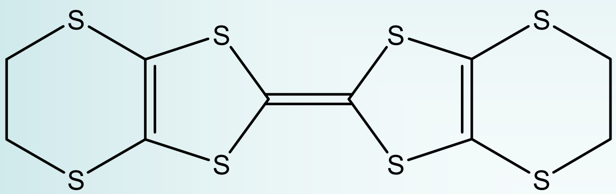
The Structure of TTF-TCNQ

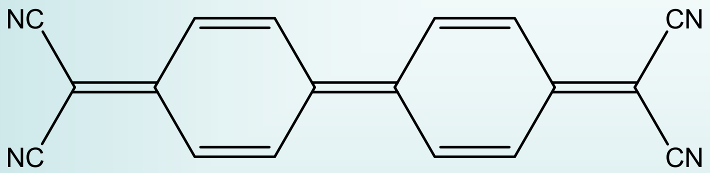


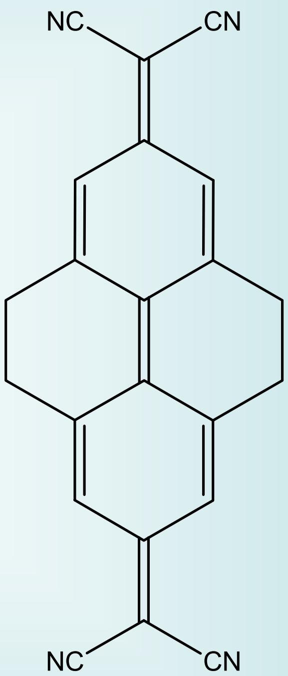
A Problem with Transport in a ½ Filled Stack (Band)



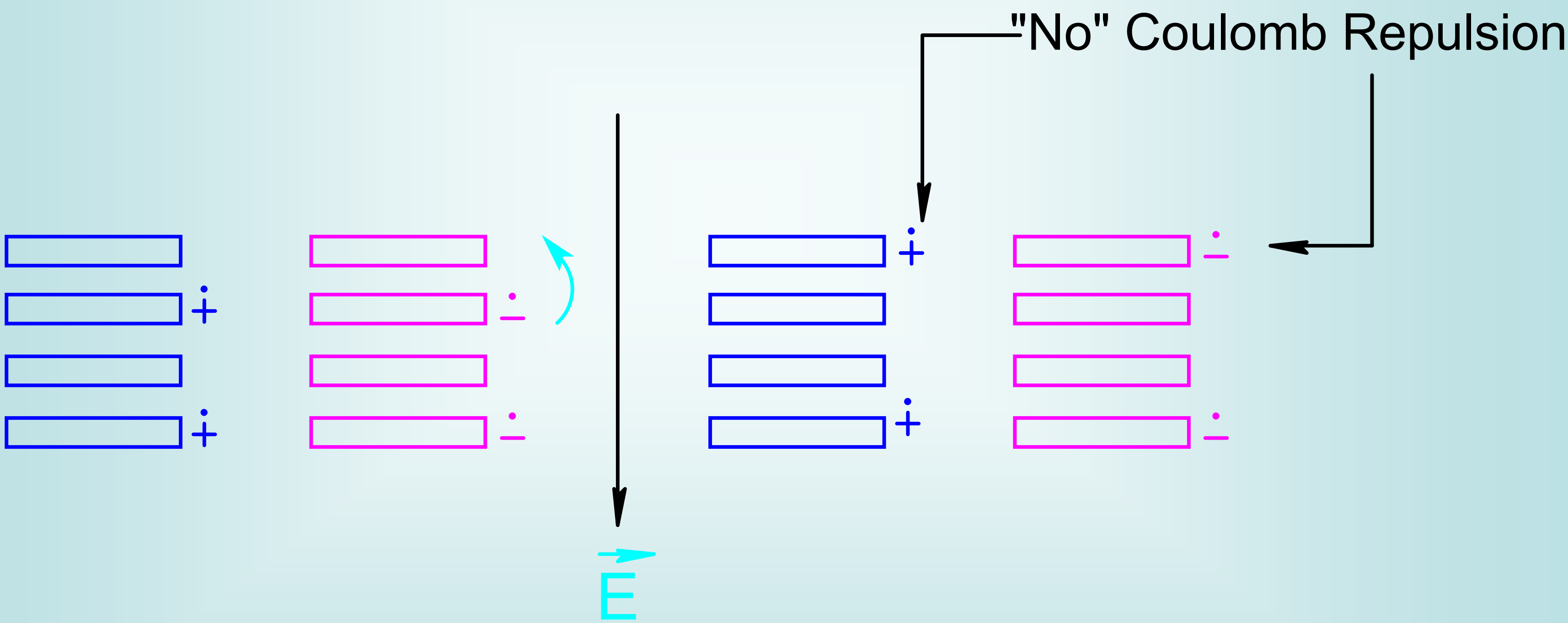
Responding to Physicists Recipes



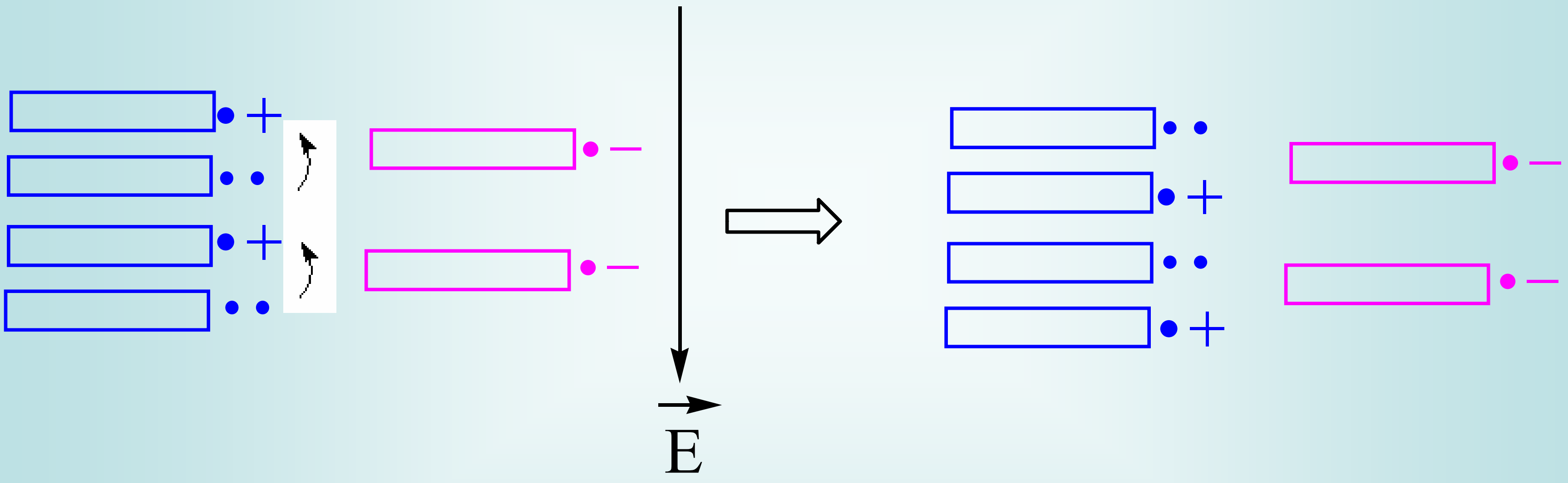




Soos-Torrance Model
(Mixed Valence)

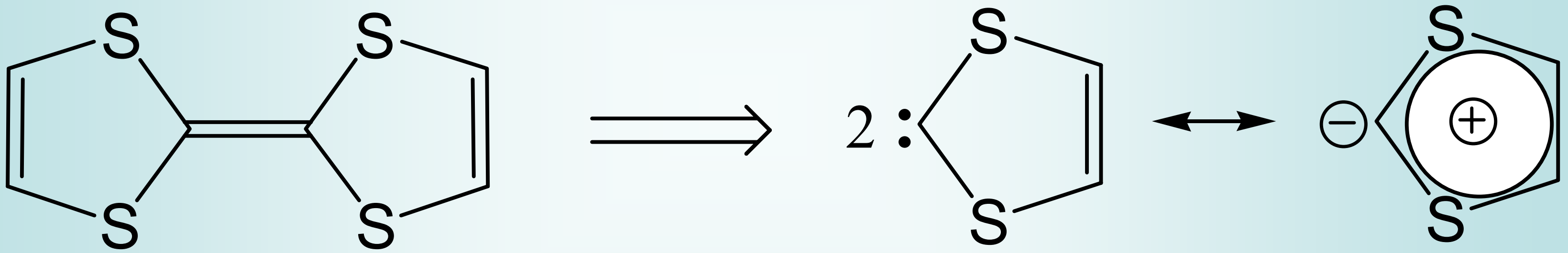


Facile Conductivity in Complex Salts of TCNQ

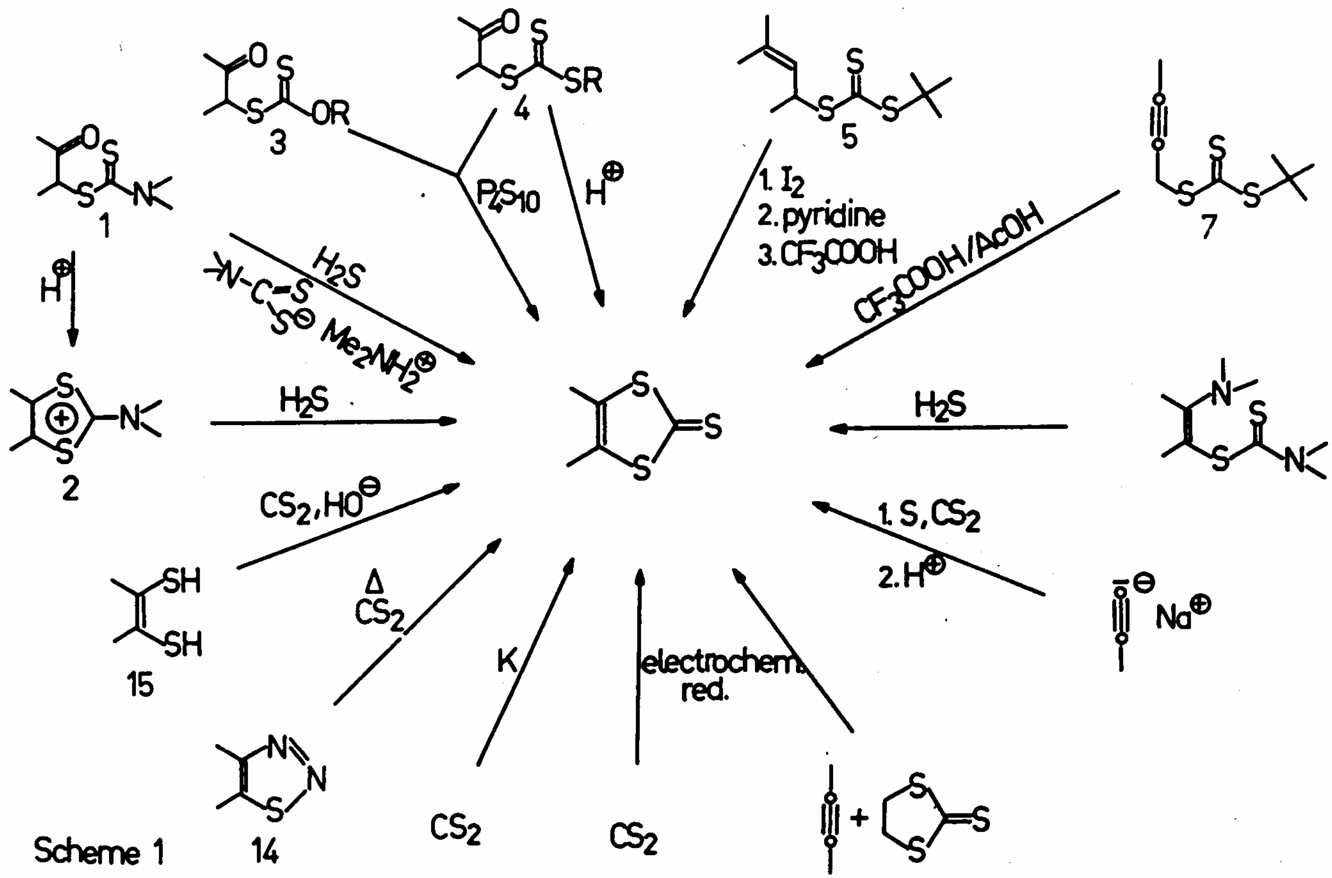


Synthesis of TTF and Derivatives

Strategy

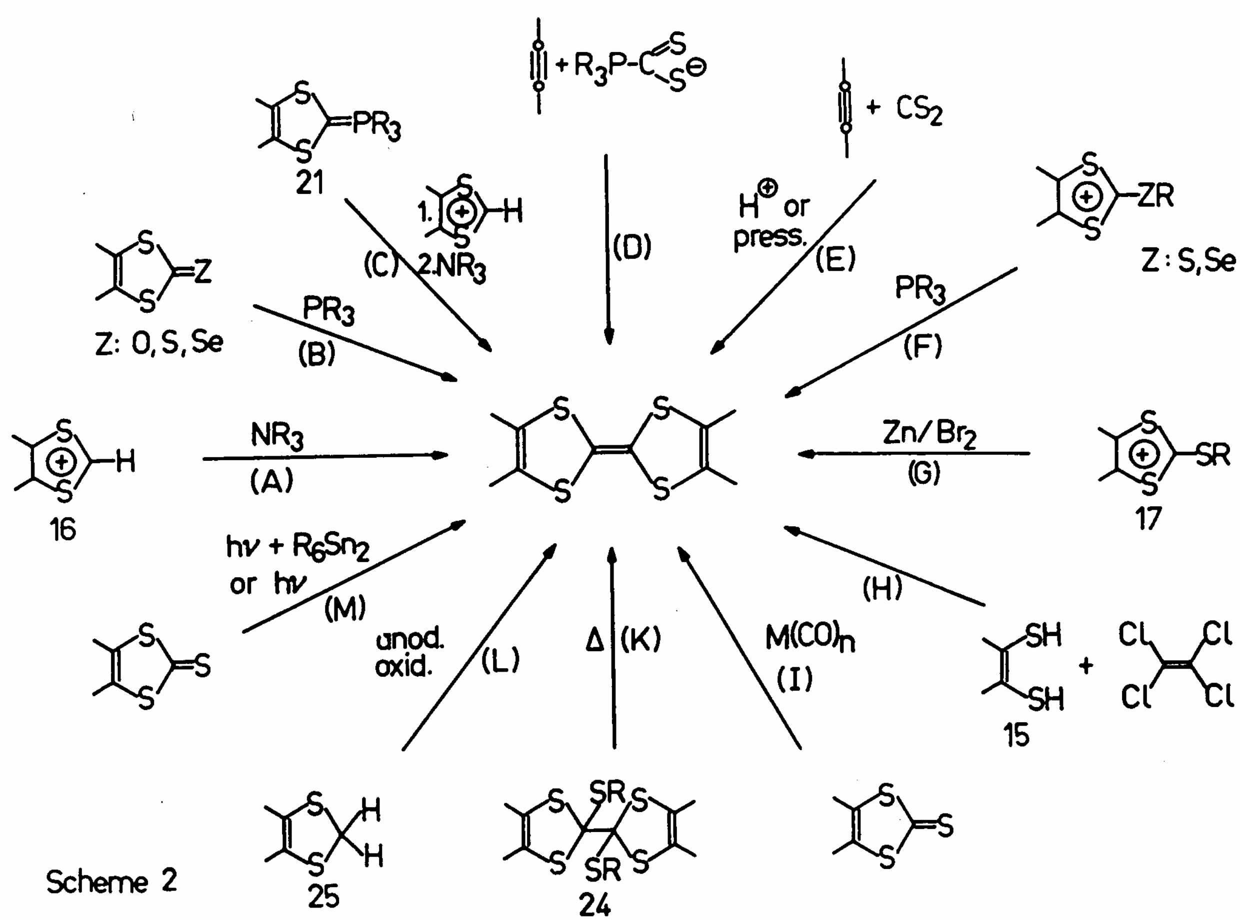


Synthesis of 1,3-Dithiole-2-thiones



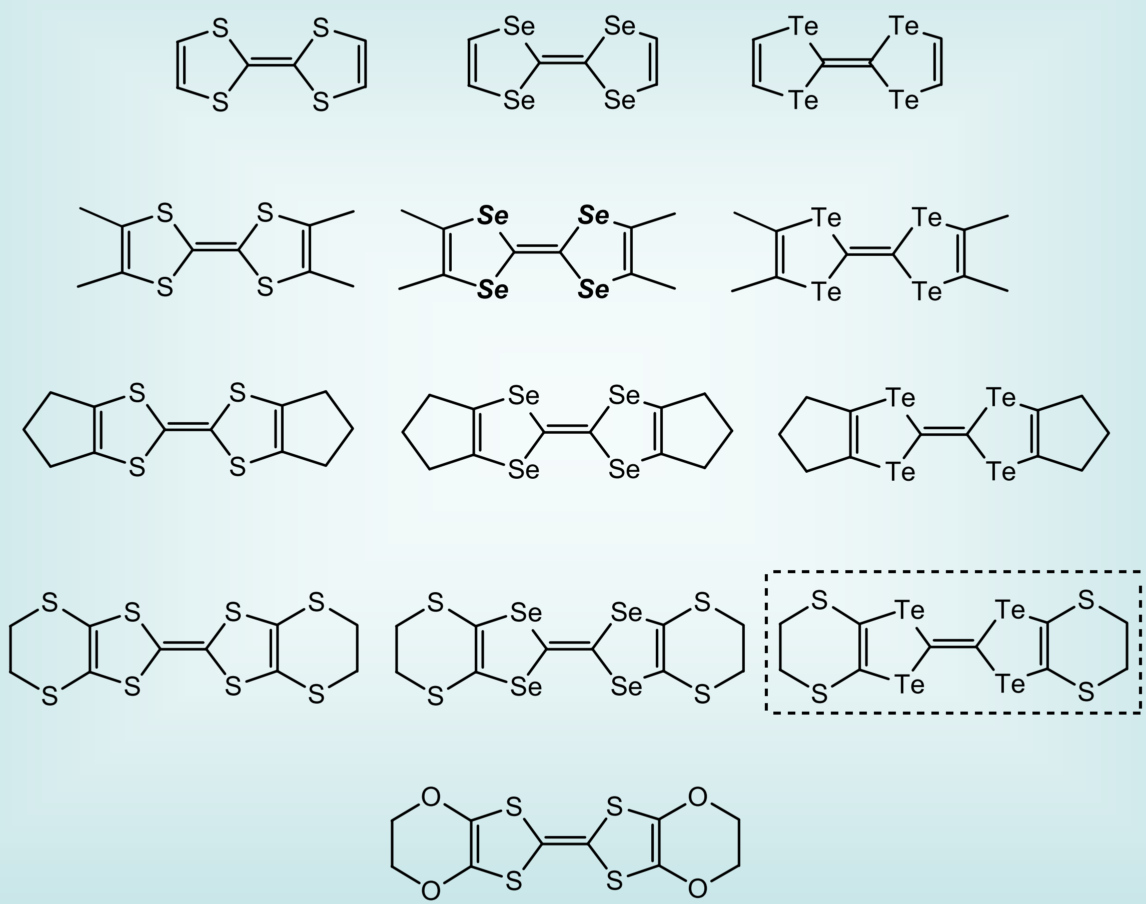
Schukat, G.; Richter, A.M.; Fanghänel, *Sulfur Reports*, **1987**, *7*, 155 - 240

Synthesis of TTFs



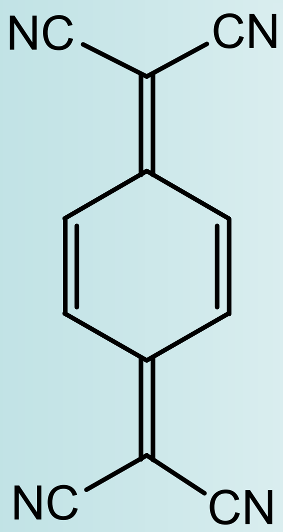
Schukat, G.; Richter, A.M.; Fanghänel, *Sulfur Reports*, **1987**, *7*, 155 - 240

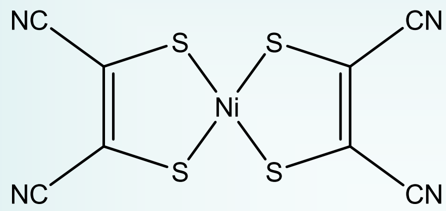
The Most Popular and Unusual Tetrachalcogen Fulvalenes



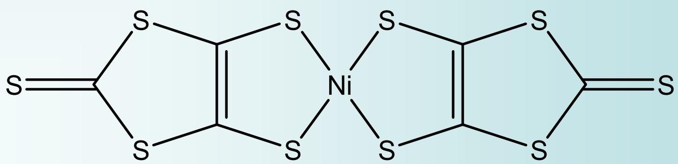
S, ***Se*** = Superconducting; ⬚ = not yet prepared

The Most Popular Acceptors





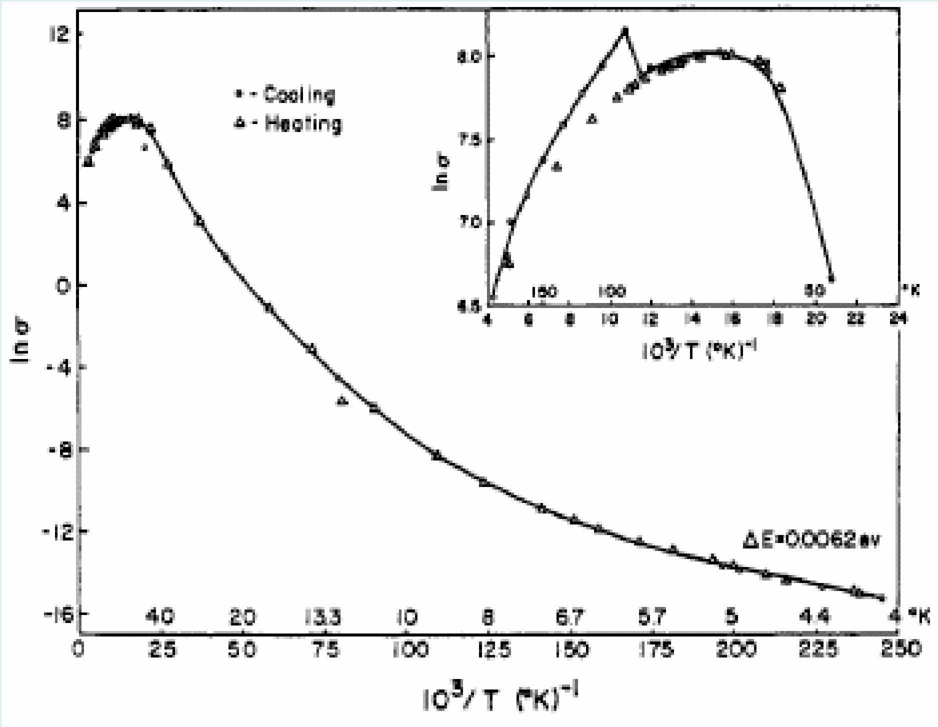
mnt



dmit

Metal Dithiolenes

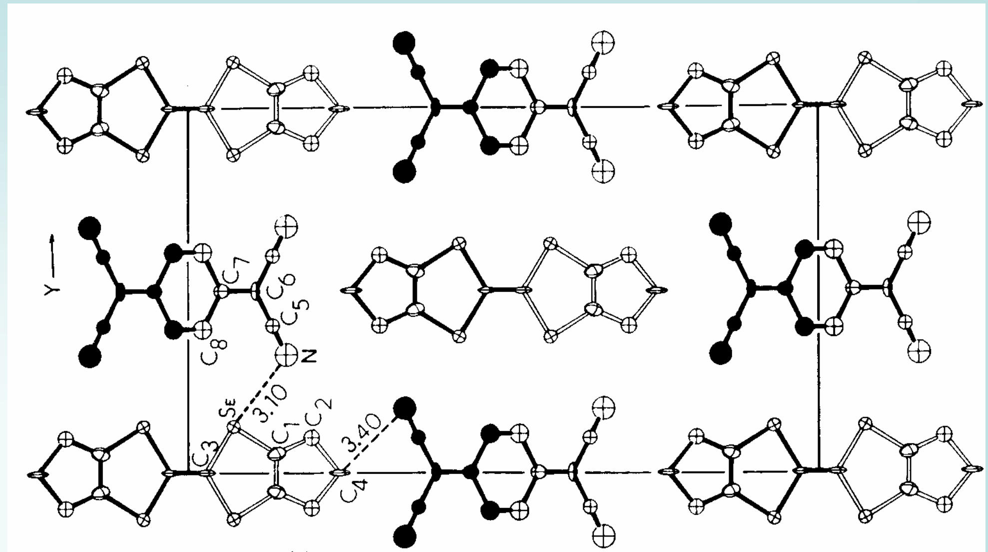
TTF-TCNQ, The First Organic Metal ?

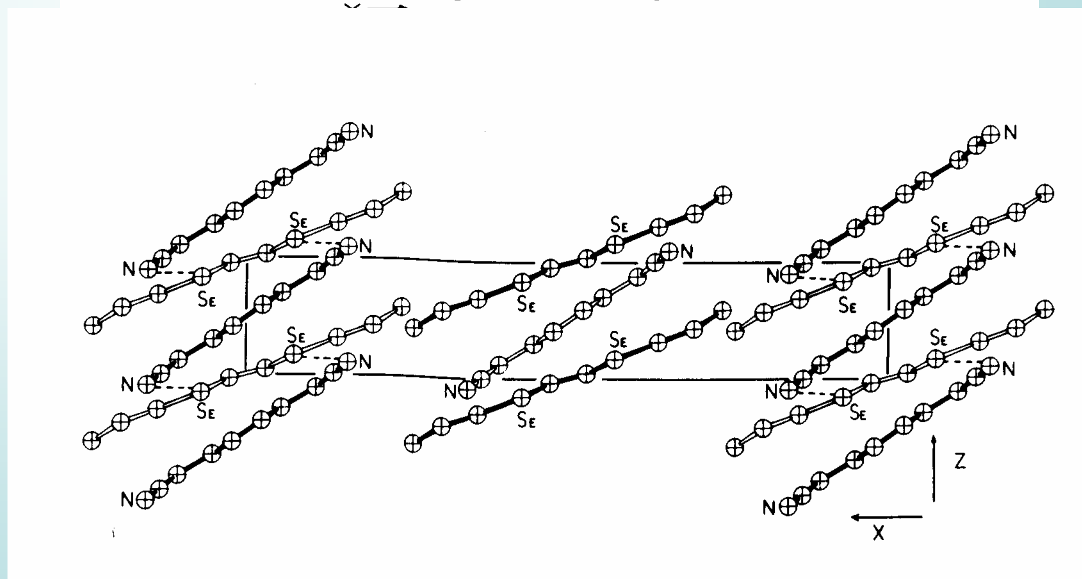


Why the loss in conductivity?

Dealing with the Peierls Catastrophe: Increase in Dimensionality and Disorder

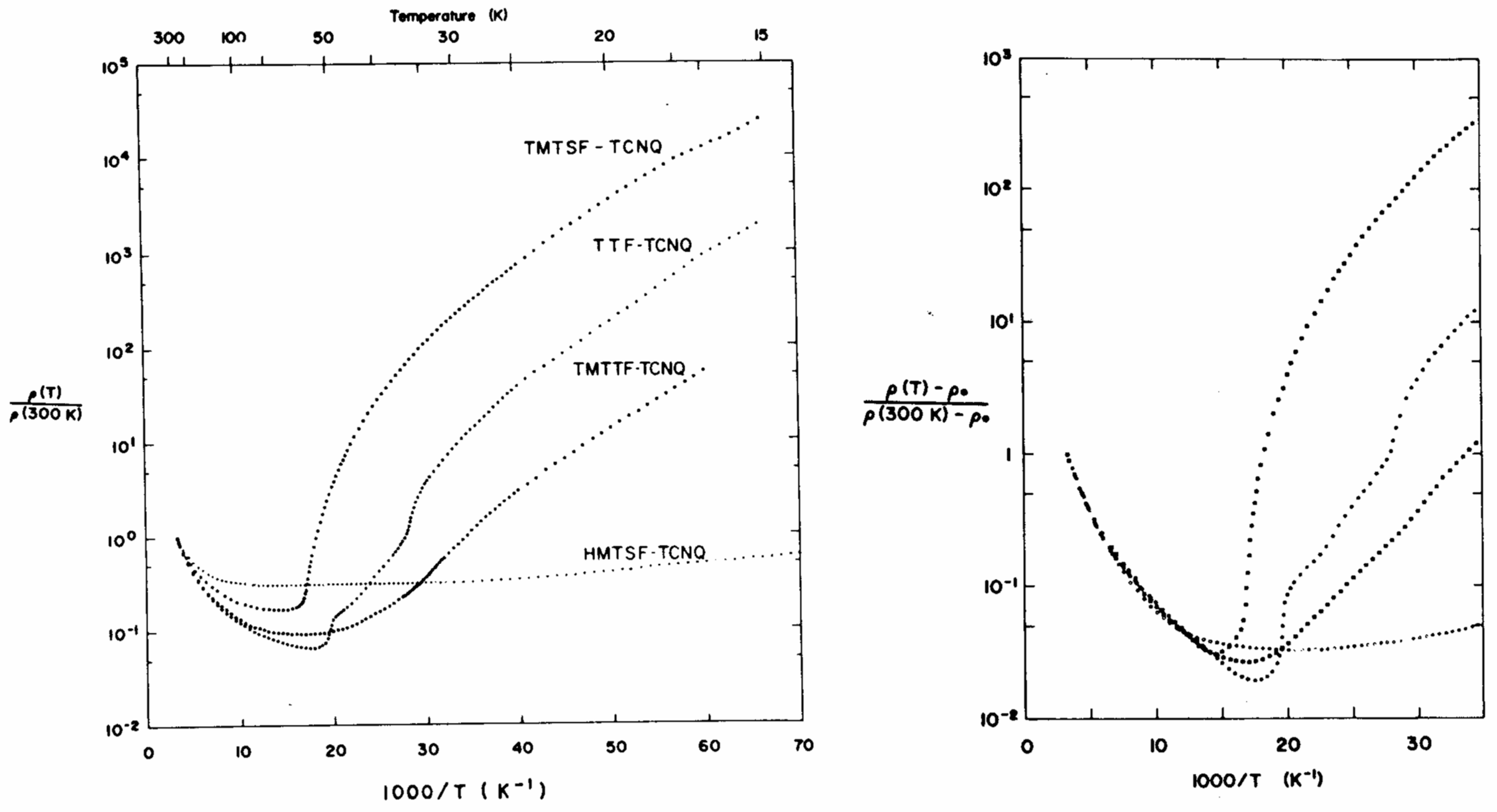
HMTSF-TCNQ





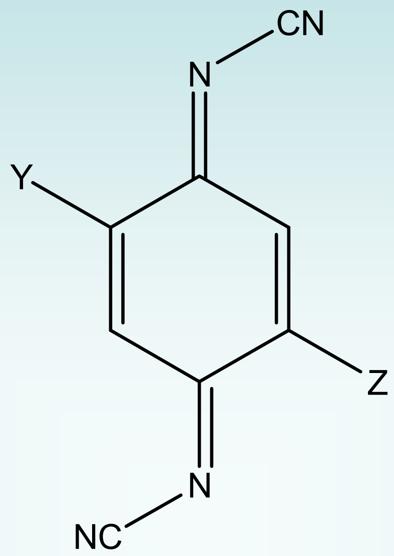
Bloch, A.N.; Carruthers, T.F.; Poehler, T.O.; Cowan, D.O. in “Chemistry and Physics of One-Dimensional Metals, Keller, H.J., Ed; Plenum, NY 1977; pp 47 -85

Comparative Temperature-Dependent Resistivities



Bloch, A.N.; Carruthers, T.F.; Poehler, T.O.; Cowan, D.O. in "Chemistry and Physics of One-Dimensional Metals, Keller, H.J., Ed; Plenum, NY 1977; pp 47 -85

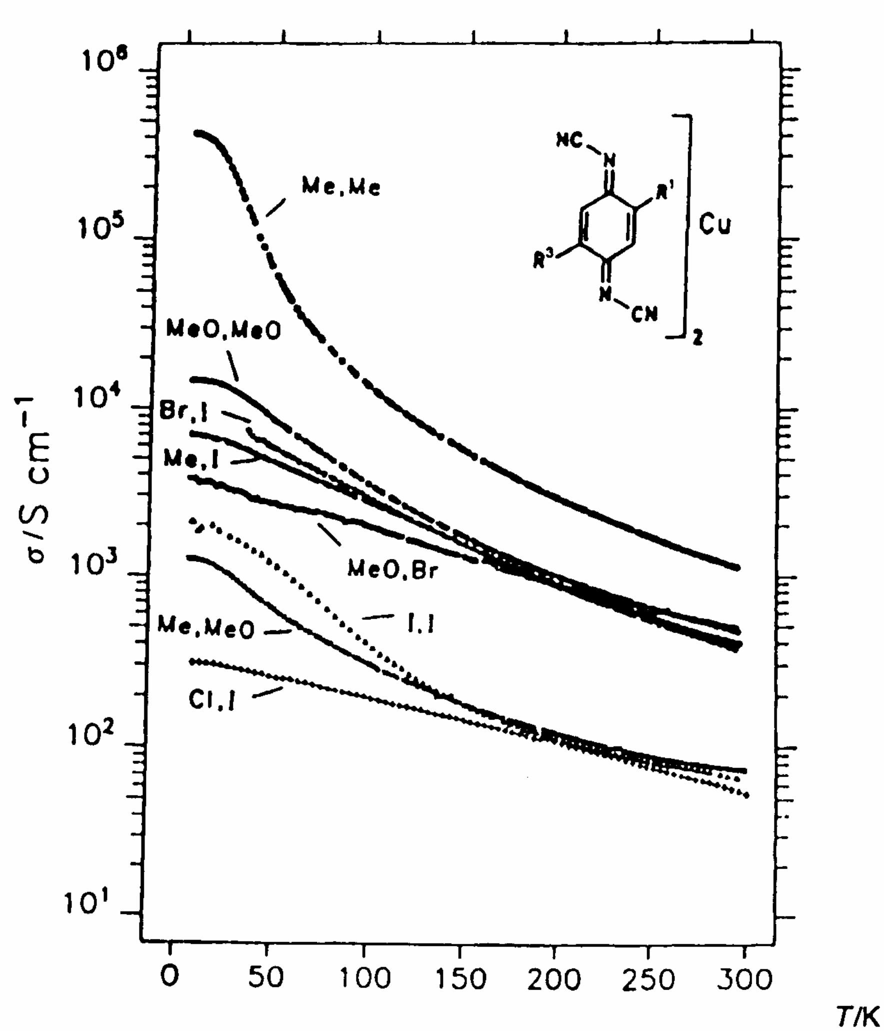
The DCNQI Story: A Truly 3-D Molecular Metal



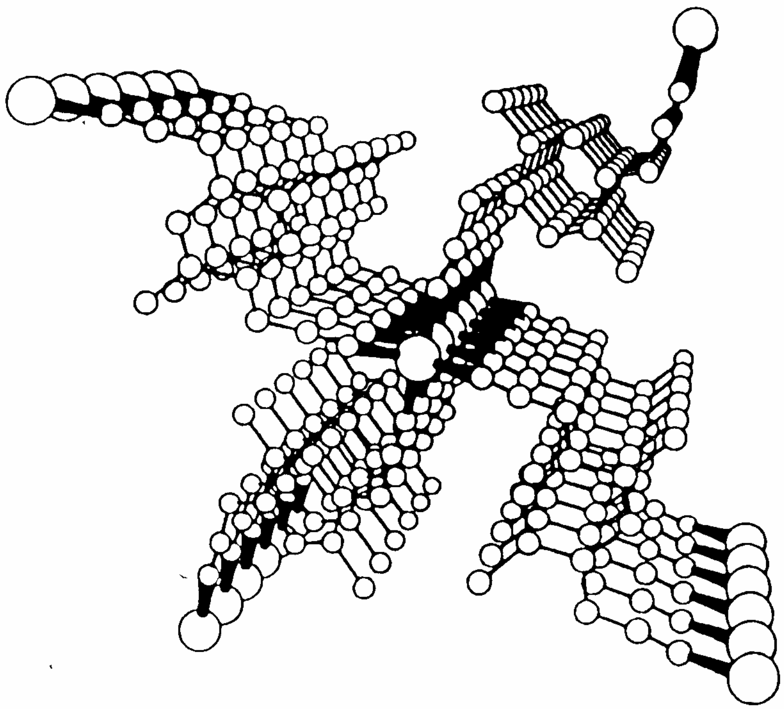
Y = Z = Me
Y = Br, Z = I
Y = Z = I
Y = Cl, Z = I
Y = Z = MeO
Etc, etc

Hünig, S. *J. Mat. Sci.* **1995**, *5*, 1469 - 1480

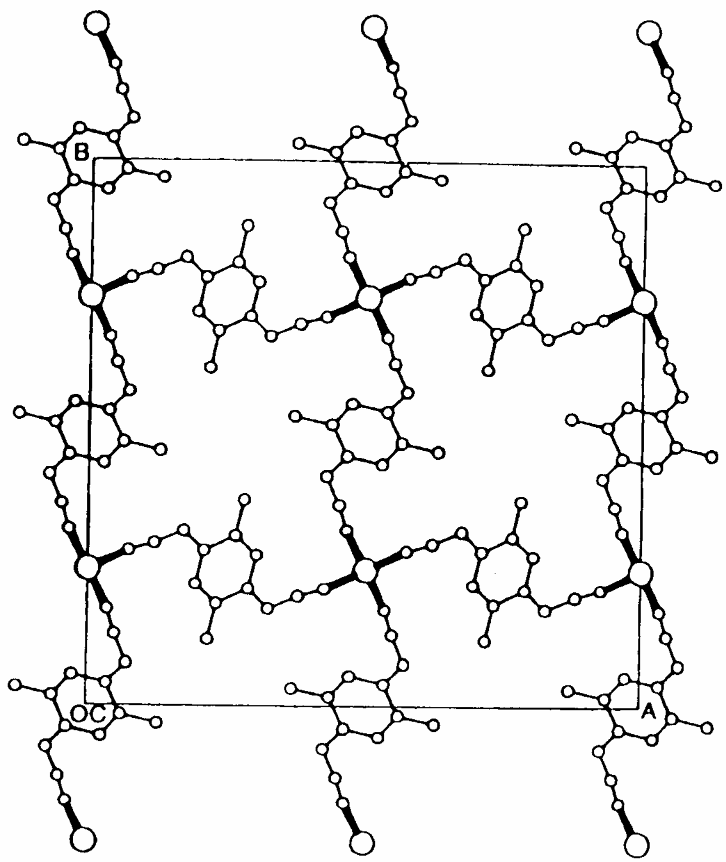
Temperature Dependence of the Conductivity Of the Copper Complexes



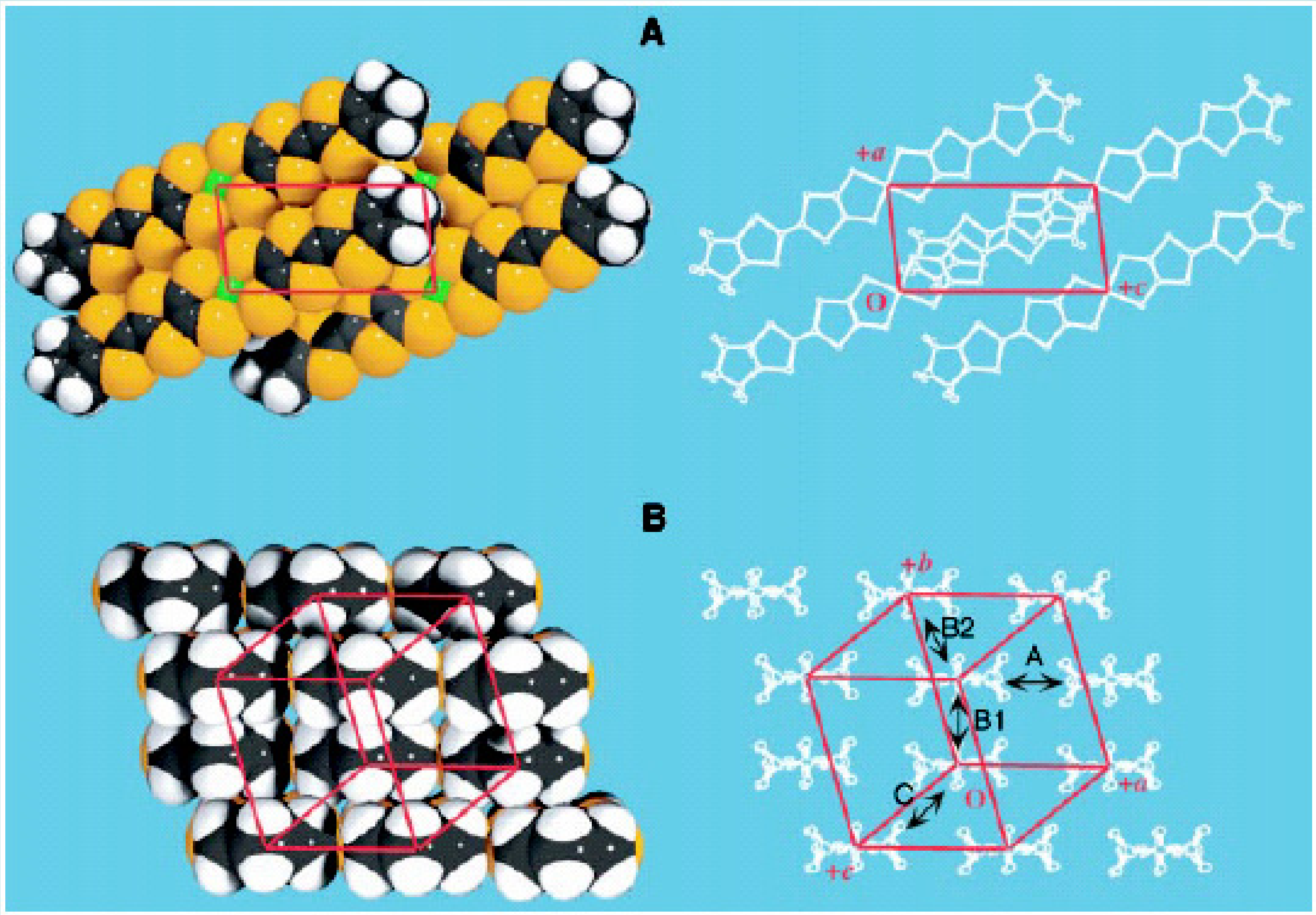
Copper-Mediated 3-Dimensionality



View of a Single Layer

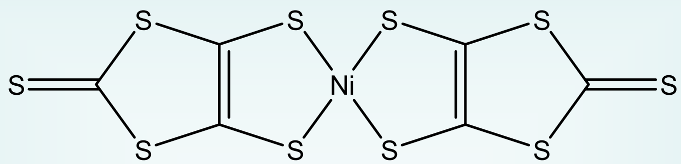


A Molecular Metal Designer's Dream: The Single Component Metal



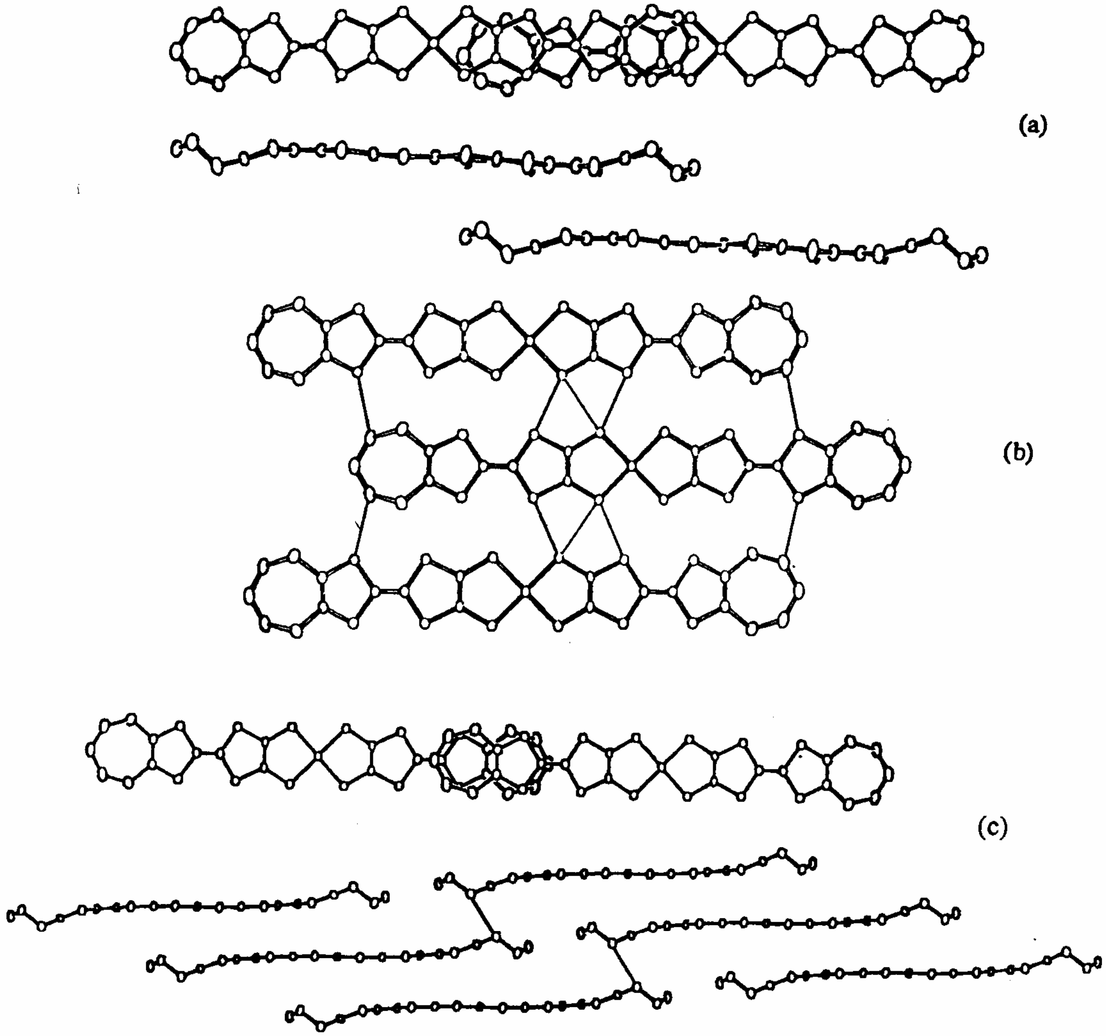
Hisashi Tanaka, Yoshinori Okano, Hayao Kobayashi, Wakako Suzuki, Akiko Kobayashi* *Science*, **2001**, *291*, 285.

The Key Building Block

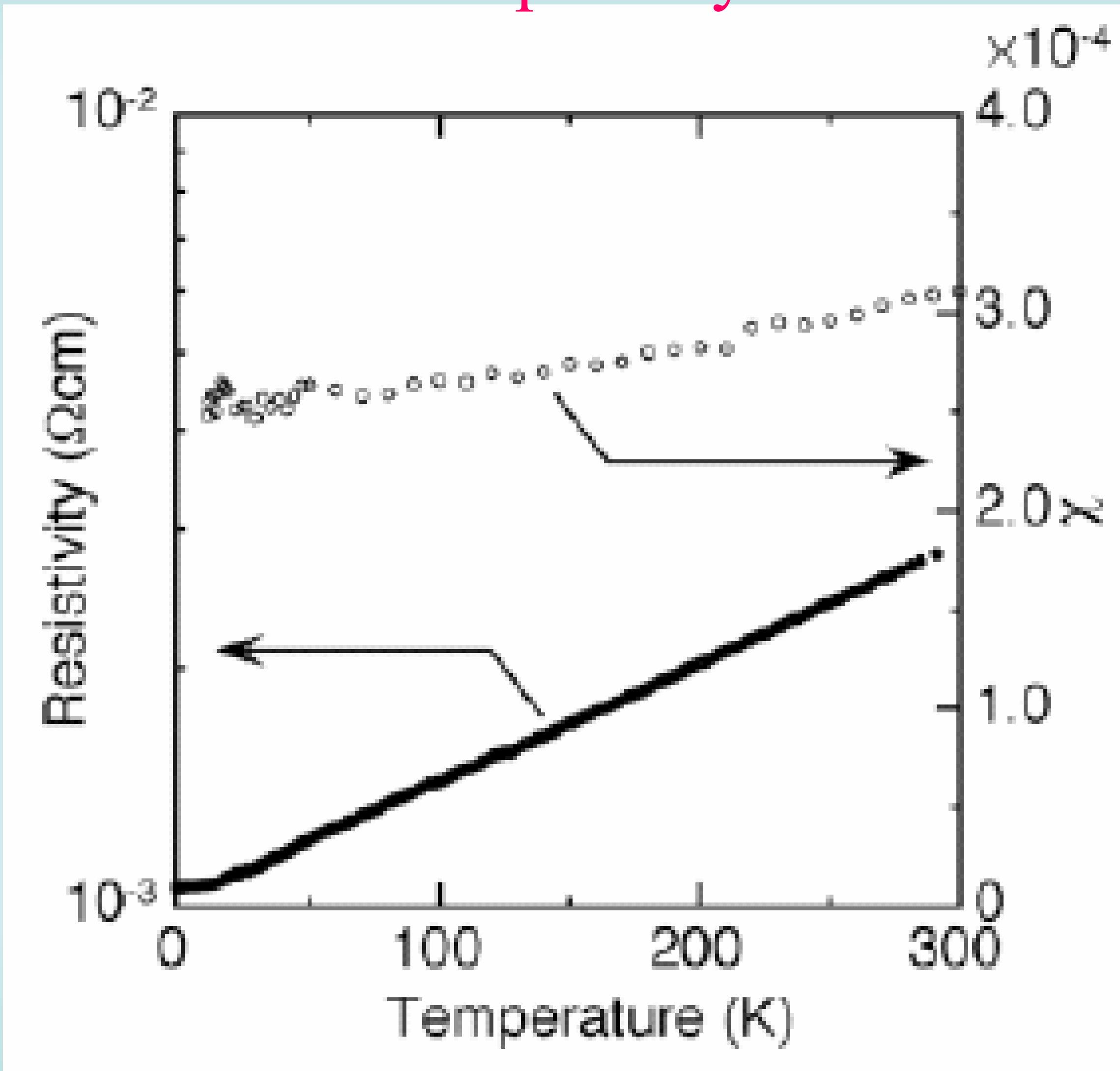


dmit

Metal Dithiolenes

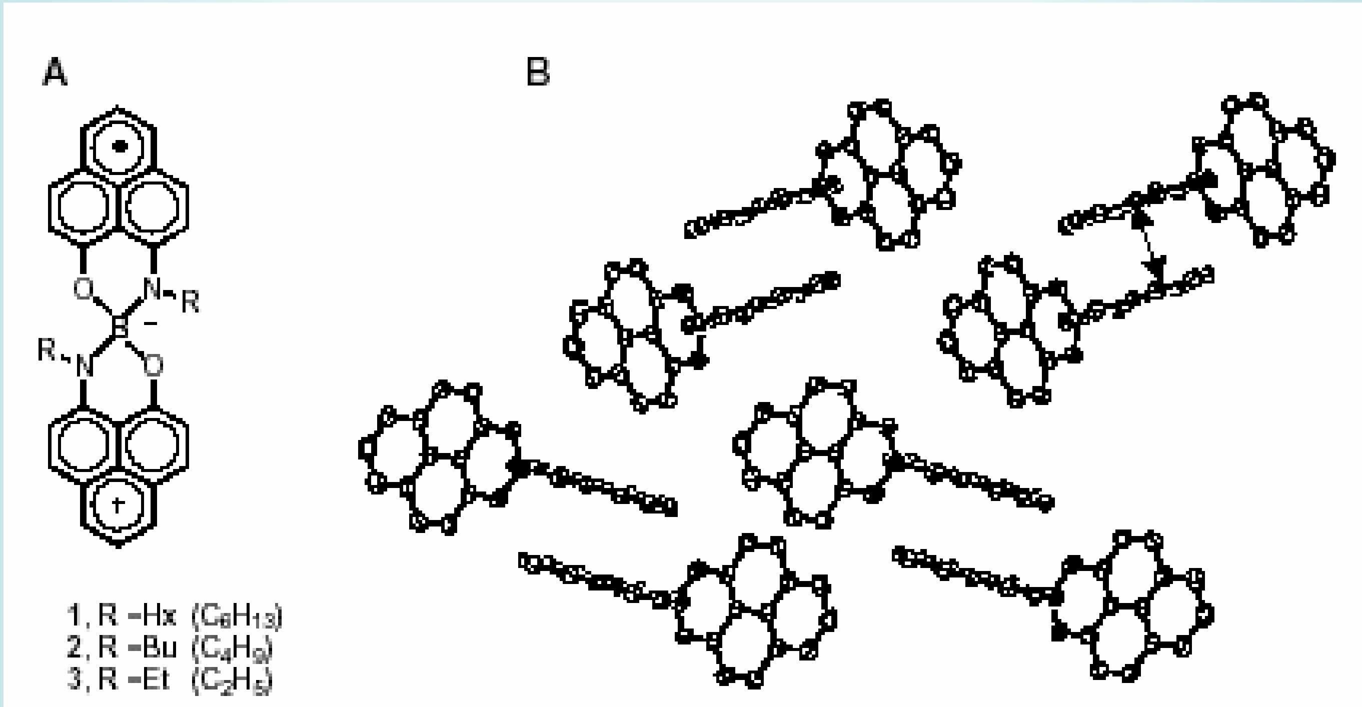

(a)
(b)
(c)

Temperature Dependence of the Resistivity & Magnetic Susceptibility



Hisashi Tanaka,1 Yoshinori Okano,1 Hayao Kobayashi, Wakako Suzuki, Akiko Kobayashi*
Science, **2001**, *291*, 285.

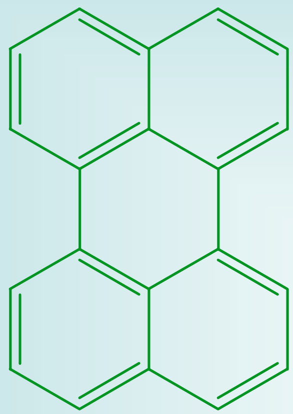
Another Single-Component Conductor



M. E. Itkis, X. Chi, A. W. Cordes, R. C. Haddon, *Science*,**2002**, *291,* 1443.

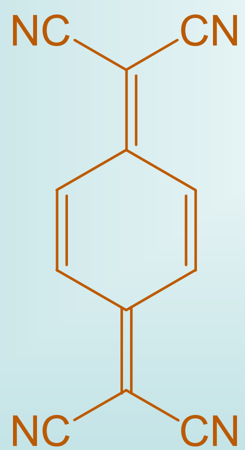
Take Home Messages from this Lesson

1.



Perylene (Per)

facile oxidation = *p*-doping



TCNQ

facile reduction = *n*-doping

Take Home Messages from this Lesson

2.

Need charge AND unpaired Spin to observe high conductivity

Summary

Organic materials based on molecular solids, while showing conductivities as high as those of some traditional metals, also exhibit other very unusual properties.

The lessons learned from organic metals apply directly to conducting polymers

The End

Thanks!

Discussion

Coffee!

David Walba

The "Giant Conductivity Peak" Phenomenon

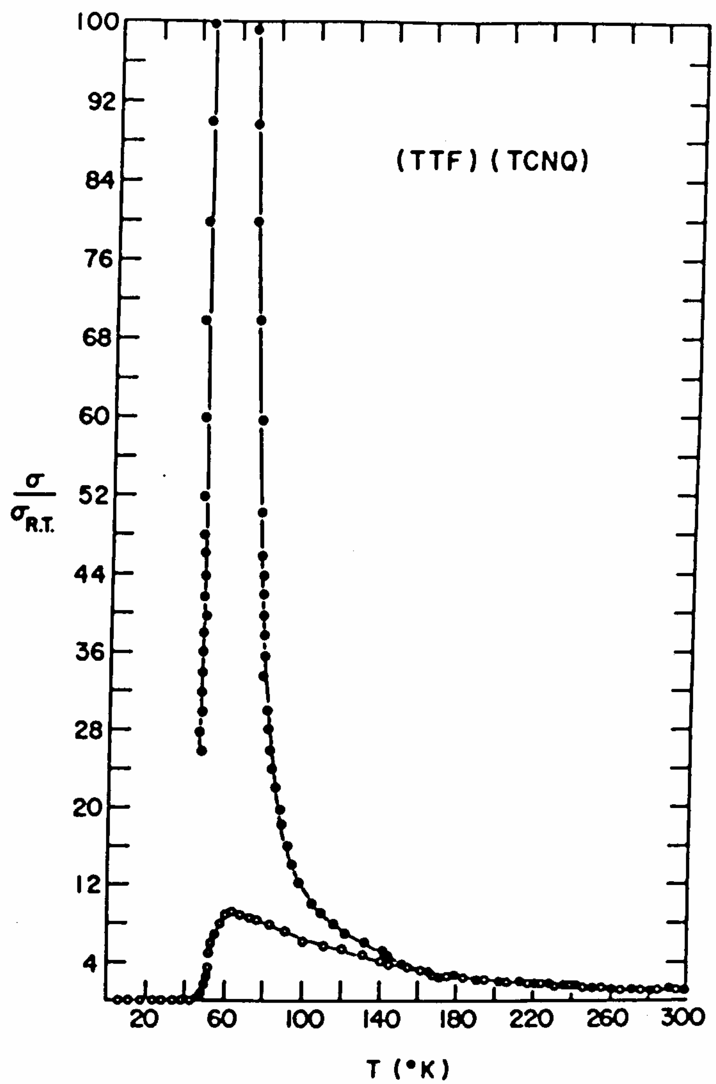


FIG. 3. Temperature dependence of the conductivity of (TTF) (TCNQ) single crystal (– ● – ● –) and of (TTF) (TCNQ) typical crystals (– ○ – ○ –).

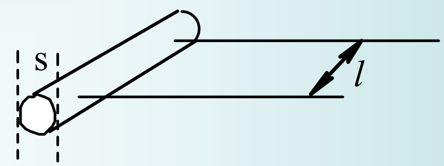
Coleman, et al, *Sol. State Commun.* **1973**, *12*, 1125 - 1132

The Measurement of Conductivity

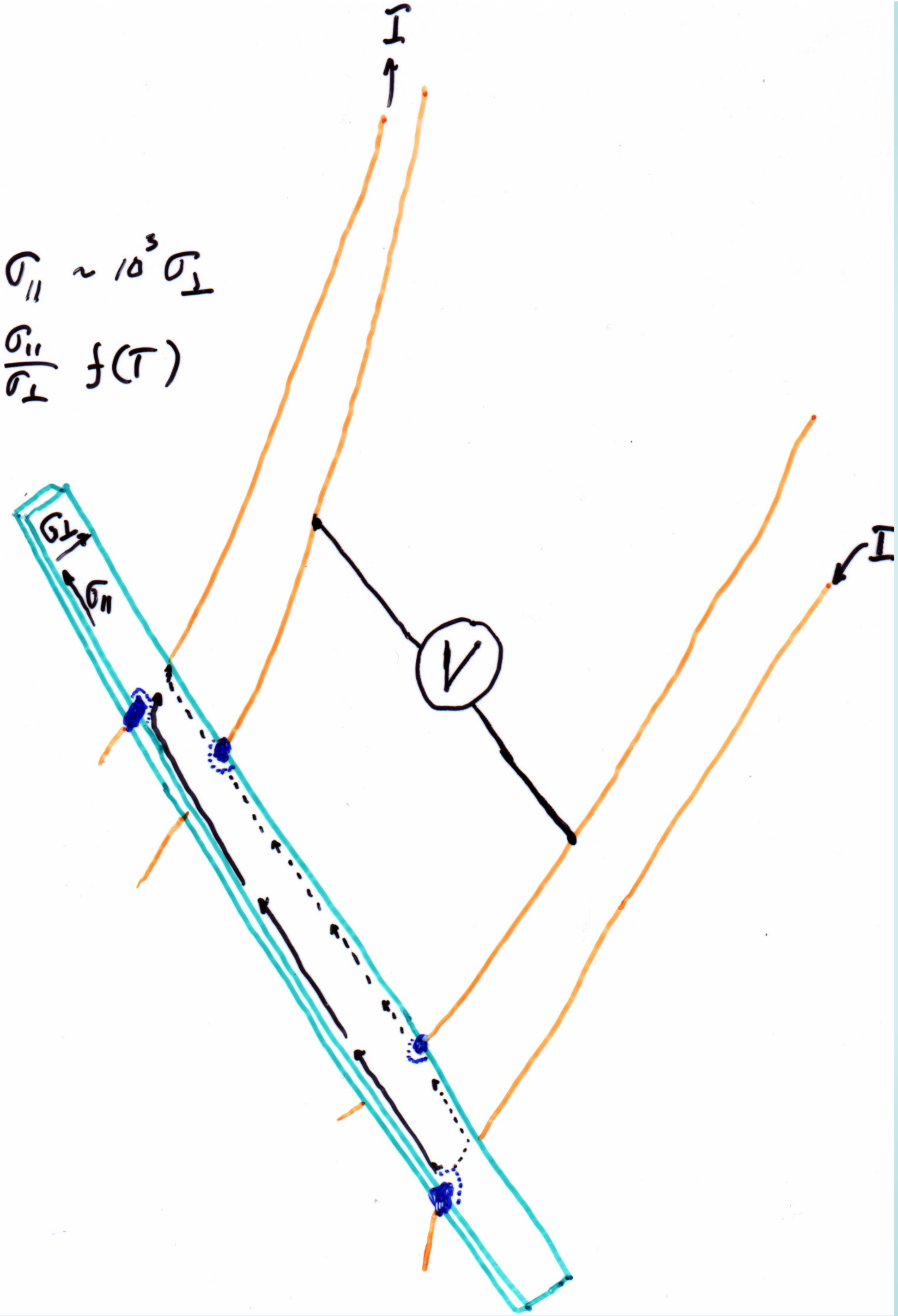
$$R = \frac{V}{i}$$

$$R = \frac{\rho l}{s}$$

$$\sigma = \frac{1}{R}$$



R = resistance, V = Potential difference,
i = current, ρ = resistivity, σ = conductivity,
s = cross sectional area



$\sigma_\parallel \sim 10^3 \sigma_\perp$
$\frac{\sigma_\parallel}{\sigma_\perp} f(T)$
I
V
I
$\sigma_\perp$
$\sigma_\parallel$